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Study of Embrittlement of the 2.25Cr-1Mo-V Steel Weld Metal by Hydrogen Charge and High Pressure Hydrogen Gas Environment

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Abstract

It is well-known that hydrogen would accumulate at internal defects of pressure vessels during shutdown and hydrogen embrittlement occurred. However it has not been clear that the effect of hydrogen gas environment for 2.25Cr-1Mo-V steel (22V) weld metal. For this reason, the purpose of this work is to identify and understand the potential for embrittlement of the 22V steel by hydrogen charge and high pressure hydrogen gas environment.

Therefore, rising load test was carried out in this study to examine the effect of dissolved hydrogen by high temperature, high pressure hydrogen exposure and high pressure hydrogen gas environment on hydrogen embrittlement at room temperature (R.T.) and 150℃. 22V forged steel base metal was used and welding was conducted by submerged arc welding (SAW) process. High and low toughness weld metals were prepared by changing PWHT condition and notch location in order to consider variation of product's weld metal.

From rising load test results, hydrogen gas environment had effect on the embrittlement of the 2.25Cr-1Mo-V steel weld metal. In contrast, dissolved hydrogen had little effect on the embrittlement. Moreover, K_{IH} value of high toughness weld metal (K_{IH} value is about 90 MPa√m) was higher than that of low toughness (K_{IH} value is about 70 MPa√m) at RT. However, K_{IH} value of low toughness weld metal was the similar level (K_{IH} value is about 110 MPa√m) of high toughness weld metal at 150℃.

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Keywords: 2.25Cr-1Mo-V steel; Hydrogen embrittlement; Weld metal

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1. Introduction

Since the heavy wall petroleum pressure vessel are operated at high temperature and high pressure hydrogen service, internal hydrogen embrittlement (I.H.E.) and hydrogen gas environment (H.E.E.) is necessary for the pressure vessel's operating procedure and startup/shutdown management. In general, I.H.E and H.E.E. mechanism of steels and metals has been reported as follows [1]. I.H.E. is the phenomenon which the embrittlement will recover by dehydrogenation. It is considered that the embrittlement happened by hydrogen atoms absorbed internal metal. The phenomenon such as a delayed fracture of a high tensile strength bolt, a cold cracking of weld metal, and a white spot are known for many years. It is well known as embrittlement of the petroleum pressure vessels operated in a high temperature, high-pressure hydrogen environment and it occurs in around room temperature after shut down. On the other hand, H.E.E. is the embrittlement by the hydrogen absorbed from the gas by metal deformation and it is the characteristic phenomenon in high pressure hydrogen gas environment. The accident which will produce a crack in NASA the first half of the 1960s on the tank for high-pressure storage made from 18%Ni Maraging steel. If stress is applied to steel and plastic deformation occurs, the newly-formed unoxidized steel surface which was not in contact with environment will be exposed, and hydrogen gas adsorbs and invades into the steel. It is considered that the dislocation makes contact and dissociation with hydrogen easy. H.E.E. is related with the dislocation mobility [2].

I.H.E. of 22V steel is generally recognized by previous studies [3,4] that K_{IH} values are strikingly decreased by hydrogen charge. However, it has not been examined that the effect of H.E.E. on K_{IH} of 22V steel, especially weld metal. It was recognized that hydrogen would accumulate at an internal defect like welded structural discontinuities of pressure vessel during shutdown. Thus, it is important to confirm hydrogen embrittlement phenomenon of 22V weld metal in order to determine minimum pressurization temperature (MPT) of hydroprocessing reactor. Accordingly, the purpose of this research is to identify and understand the effect of hydrogen gas environment on the embrittlement of the 22V steel weld metal.

2. Experimental Procedures

2.1. Material

The chemical composition of weld metal is shown in Table 1. Base metal was used 22V forged steel and welding process was submerged arc welding (SAW). Groove geometry of test block is described in Fig. 1 and welding condition was shown below. Current: 500-600A Voltage: 27-34V and Speed: 600-700mm/min. After welding, sample was treated de-hydrogen heat treatment (DHT) of 350oC for 2hrs. Moreover, it was examined that there is no harmful defect in the weld by ultrasonic testing (UT) and surface dye penetrant testing (PT). After the non-destructive examinations, sample was cut into coupon 1 and 2. Test coupon 1 was called high toughness weld material was treated PWHT of 705oC for 8hrs. Test coupon 2 was called low toughness weld which PWHT of 680oC for 8hrs carried out in order to prepare different material of toughness.

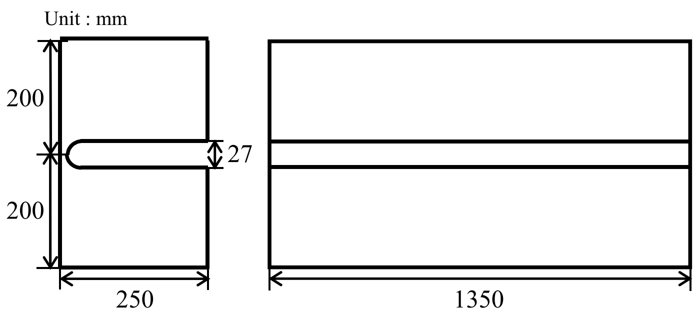


Fig. 1. Groove geometry of test block.

Table 1. Chemical composition of weld metal (mass%).

C	Si	Mn	P	S	Ni	Cr	Cu	Mo	V	N (ppm)	J-Factor
0.09	0.13	1.07	0.004	0.002	0.07	2.39	0.09	1.05	0.35	85	84

J-Factor = (Si + Mn)(P +S) x 10^4 / mass%

2.2. Experimental method

In order to introduce aiming 10ppm hydrogen inside of the weld metal, the hydrogen charging condition was 450ºC, 25MPa hydrogen gas pressure and the exposed time for 48h by autoclave was shown in Fig. 2. The specimens were rapidly taken out from the autoclave after hydrogen exposure and then cooled to water bath. After the specimens cooled to room temperature, rising load test and holding load test were conducted.

Fig. 2. Autoclave for hydrogen charging.

Table 2. Rising load test condition.

Material	Hydrogen Charge	Test Environment	T.P. No.
High Toughness	None	Air	H-N-A
		20MPa H_2Gas	H-N-G
	10ppm (Aiming)	Air	H-H-A
		20MPa H_2Gas	H-H-G
Low Toughness	None	Air	L-N-A
		20MPa H_2Gas	L-N-G
	10ppm (Aiming)	Air	L-H-A
		20MPa H_2Gas	L-H-G

K_{IH} value of each specimen was evaluated by rising load test. Specimen type of rising load test was 1T-C(T) (ASTM E 1820) described in Fig. 3. Schematic illustration of specimen location was shown in Fig. 4. Notch location was weld center for high toughness weld material and quarter width of weld metal for low toughness weld metal. The test condition was shown in Table 2 which test temperature was room temperature (R.T.) and 150ºC, hydrogen charge was carried out aiming hydrogen content 10ppm and test environment was air and 20MPa hydrogen Gas. The test was conducted at a rate of 0.01mm/min (K=1.3×10^{-2} MPa √m/s) which was minimum limit of machine. After rising load test, specimen was opened in liq. N_2 and fracture surface was observed by scanning electron microscope (SEM) in order to confirm stretch zone. Hydrogen content was measured using another measurement piece after the test. K_{IH} value was calculated using the following equation (1) where P is load of deviation point, a(m) is pre-crack length, W(m) is specimen width, B(m) is specimen thickness and B_N (m) is specimen thickness at side groove.

$$K_{IH} = \frac{P\sqrt{a}}{\sqrt{BB_N W}} F_1(a/W) \tag{1}$$

$$F_1(a/W) = 29.6-18.55(a/W)+655.7(a/W)^2-1017.0(a/W)^3+638.9(a/W)^4$$

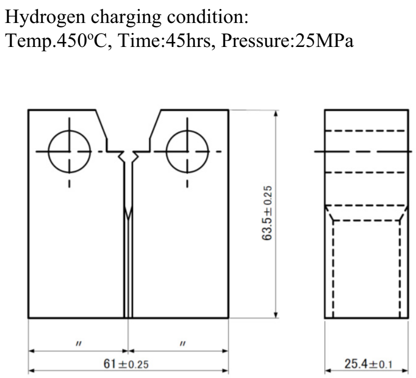


Fig. 3. Geometry of 1T-C(T) specimen.

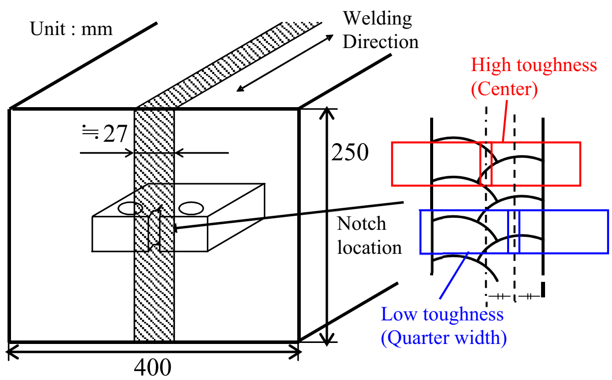


Fig. 4. Schematic illustration of specimen location.

Deviation point was determined by difference in load line displacement method as shown in Fig 5. Deviation point is that the difference in load line displacement begins to rise up. In order to check whether crack growth occurs at K_{IH} load, holding load test was carried out at RT in 20MPa gaseous hydrogen. The specimen was charged aiming 10ppm hydrogen. Holding load equivalent to K_{IH} is obtained by rising load test. In the case of high toughness weld material, holding load was 33.1kN. In the case of low toughness weld material, it was 30.1kN. Holding time was 10 days. Load was applied at rate of 0.01mm/min to aiming load, and then it was kept constant. After the test, specimen was opened in liq. N_2 and fracture surface was observed by SEM in order to confirm the area of propagated crack.

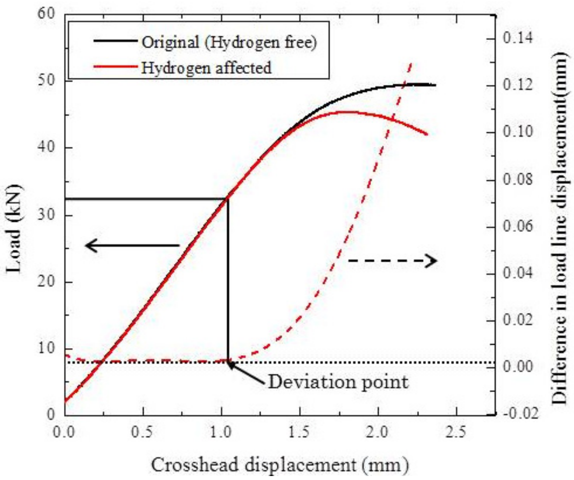


Fig. 5. Determination example of deviation point.

3. Results

3.1. Mechanical properties of high and low toughness weld metal

Table 3. Tensile test results of weld metal.

	0.2% Yield Stress (MPa)	Tensile Strength (MPa)	Elongation (%)	Red. of Area (%)
High Toughness Weld Metal	600	701	22.8	71.9
Low Toughness Weld Metal	688	775	18.1	68.1

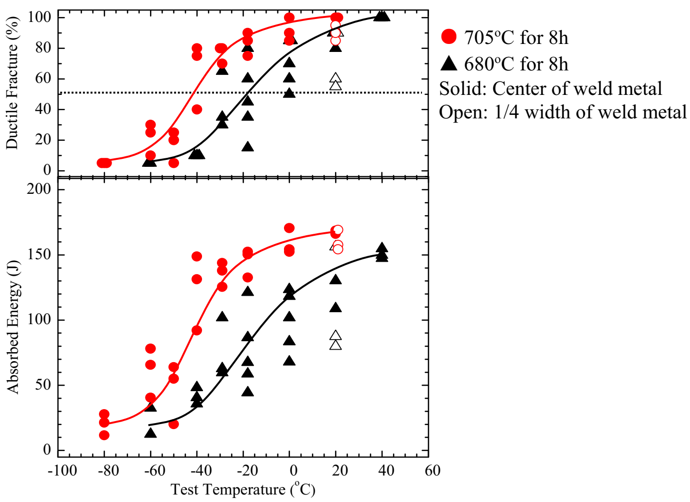
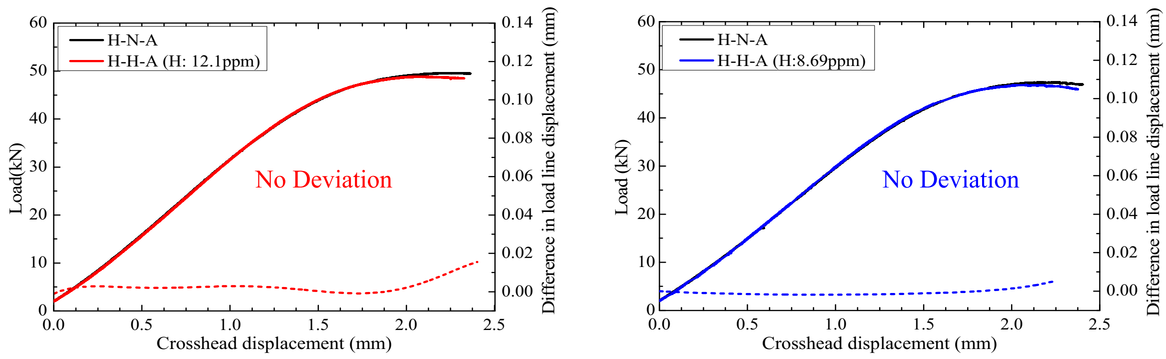


Fig. 6. Charpy transition curve of weld metal.

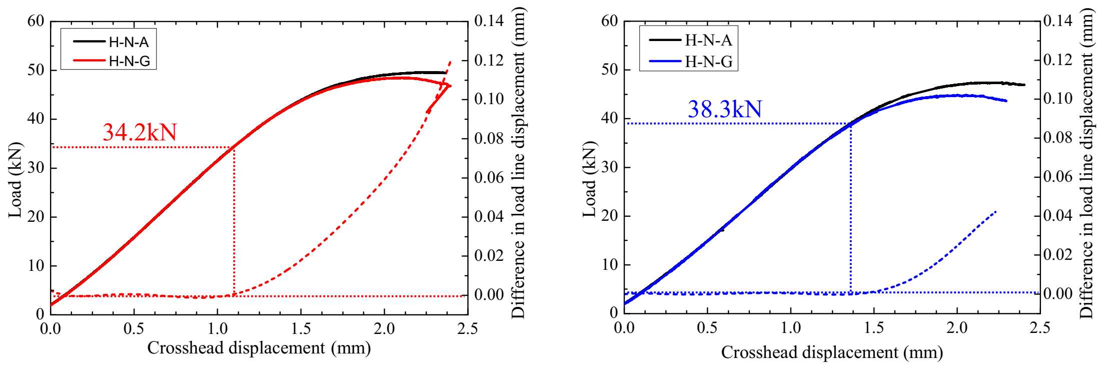
Tensile test results of high and low toughness weld metals are shown in Table 3. Tensile strength and yield stress of low toughness weld metal was higher than that of high toughness weld metal. Additionally, tensile property of high toughness weld metal that was treated usually PWHT (705ºC for 8hrs) satisfied the spec. of ASME SA-336 F22V which is for base metal. Charpy transition curve of high and low toughness weld metal is shown in Fig. 6. Fracture appearance transition temperature (FATT) was -42ºC for high toughness weld metal and it was -16ºC for low toughness weld metal. Moreover, charpy impact specimens were obtained at center and quarter width of weld metal in order to investigate the effect of notch location. It doesn't have an effect on the toughness at 20ºC for high toughness weld metal but the toughness of quarter width of weld metal decreased compared with the center of weld metal for low toughness weld metal. From these results, 705ºC for 8hrs and center of weld metal were determined as PWHT condition and notch location for high toughness weld metal. On the other hand, 680ºC for 8hrs and one-quarter width of weld metal were determined as PWHT condition and notch location for low toughness weld metal to clarify the influence of material toughness on the K_{IH}.

3.2. Rising load test results of high toughness weld metal



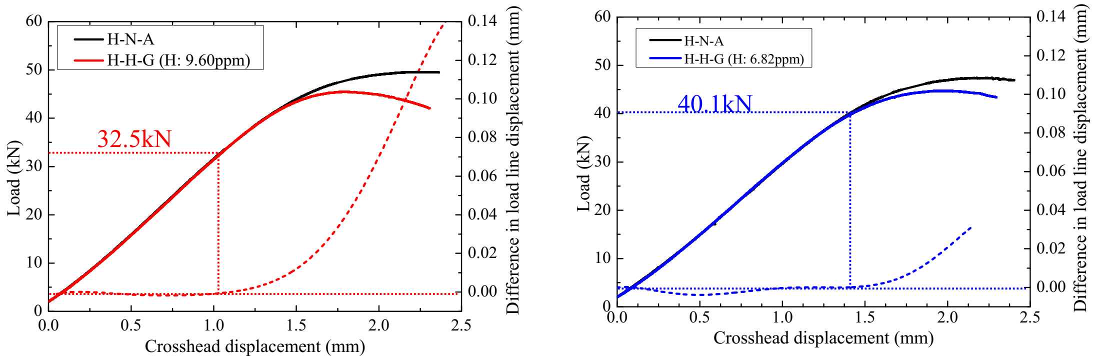
(a) (b)

Fig. 7. Rising load test results of T.P.No. H-N-A and T.P.No. H-H-A. (a) at R.T.; (b) at 150ºC.



(a) (b)

Fig. 8. Rising load test results of T.P.No. H-N-A and T.P.No. H-N-G. (a) at R.T.; (b) at 150ºC.

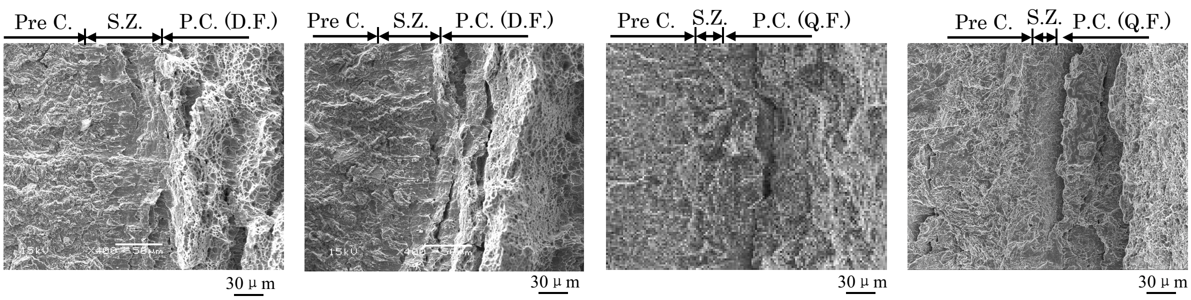


(a) (b)

Fig. 9. Rising load test results of T.P.No. H-N-A and T.P.No. H-H-G. (a) at R.T.; (b) at 150ºC.

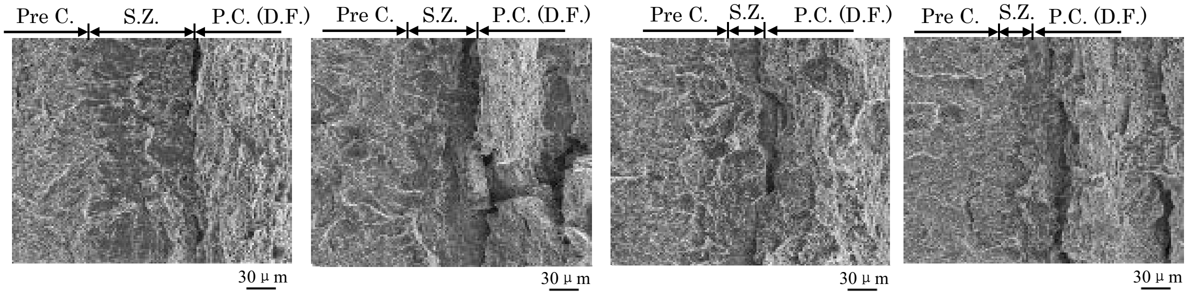
In this test, standard condition that was none hydrogen charge and air environment was used one specimen but other conditions were used two specimens (N1, N2) in order to confirm repeatability of the test. Fig. 7 shows Load, Difference in load line displacement and Crosshead displacement curves (L, D-C curve) of H-N-A and H-H-A condition at R.T. and 150ºC. Hydrogen content after rising load test of H-H-A was also shown in the figure. As shown in the figures, there is no deviation point in H-H-A because curve of difference in load line displacement was not rise up in these conditions. Fig. 8 shows L, D-C curve of H-N-A and H-N-G condition. It is clear that deviation point was observed in H-N-G specimens. K_{IH} value at R.T. that was calculated by load of deviation point was 93 MPa √ m and besides K_{IH} value at 150ºC was 105 MPa √ m. Thus, it was clear that hydrogen environment had effect on hydrogen embrittlement at both of test temperature. Fig. 9 shows L, D-C curve of H-N-A and H-H-G condition. These are indicative of effect of hydrogen charge and test environment. This figure shows there is deviation point for both specimens. K_{IH} value at R.T. that was calculated by load of deviation point was 90 MPa √ m and K_{IH} value at 150ºC was 81 MPa √ m. From these results, K_{IH} value might be insensitive to dissolved hydrogen under hydrogen gas environment.

Figures 10, 11 shows fracture appearance of each condition after rising load test. Stretch zone was precisely observed and propagated crack was ductile fracture in H-N-A and H-H-A condition. However a lot of sub-crack occurred in propagated crack of H-H-A condition. Stretch zones of H-N-G and H-H-G were slightly observed, but the width was less than that of H-N-A condition, and also quasi-cleavage appearance was observed in propagated crack by hydrogen gas environment. However stretch zone width was increased at 150ºC in comparison with that at R.T. Moreover, propagated crack morphology was changed to ductile fracture at 150ºC even if test condition was under hydrogen gas environment. On the other hand, different between H-N-G and H-H-G were not confirm in fracture surface.



Pre C.: Pre Crack, S.Z.: Stretch Zone, P. C.: Propagated Crack D.F.: Ductile Fracture, Q.F.: Quasi-cleavege Fracture

Fig. 10. SEM image of fracture surface of each condition at R.T. (a) H-N-A; (b) H-H-A; (c) H-N-G; (d) H-H-G.



Pre C.: Pre Crack, S.Z.: Stretch Zone, P. C.: Propagated Crack D.F.: Ductile Fracture, Q.F.: Quasi-cleavege Fracture

Fig. 11. SEM image of fracture surface of each condition at 150ºC. (a)H-N-A; (b) H-H-A; (c) H-N-G; (d) H-H-G.

K_{IH} values of high toughness weld metal were obtained rising load test were summarized in Table 4 and 5. Based on these results, it is evident that the effect of dissolved hydrogen on hydrogen embrittlement was a little, whereas hydrogen gas environment acts as the embrittlement factor in this condition. Therefore, K_{IH} values at both temperatures were almost same but propagated crack morphology was changed from quasi-cleavage to ductile fracture because of test temperature.

Table 4. Rising load test results of high toughness weld metal at R.T.

T.P.No.	Hydrogen content after test (ppm)	Test Environment	K_{IH} (MPa√m)	Fracture Appearance
H-N-A	—	Air	—	S.Z. D.F.
H-H-A	12.1 10.1	Air Air	No Deviation Point	S.Z. D.F.
H-N-G	— —	20MPa H_2 Gas	93 88	Q.F.
H-H-G	11.8 9.90	20MPa H_2 Gas	90 91	Q.F.

S.Z.: Stretch Zone, D.F.: Ductile Fracture, Q.F.: Quasi-cleavege Fracture

Table 5. Rising load test results of high toughness weld metal at 150ºC.

T.P.No.	Hydrogen content after test (ppm)	Test Environment	K_{IH} (MPa√m)	Fracture Appearance
H-N-A	—	Air	—	S.Z. D.F.
H-H-A	8.69 6.66	Air Air	No Deviation 110	S.Z. D.F.
H-N-G	—	20MPa H_2 Gas	105	S.Z. D.F.
H-H-G	10.5 6.82	20MPa H_2 Gas	(81) 110	S.Z. D.F.

S.Z.: Stretch Zone, D.F.: Ductile Fracture

3.3. Rising load test results of low toughness weld metal

Table 6. Rising load test results of low toughness weld metal at R.T.

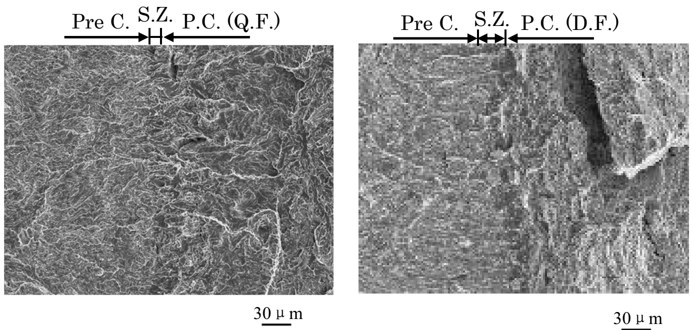
T.P.No.	Hydrogen content after test (ppm)	Test Environment	K_{IH} (MPa√m)	Fracture Appearance
L-N-A	—	Air	—	S.Z. D.F.
L-H-A	7.05 8.26	Air Air	129 116	S.Z. D.F.
L-N-G	— —	20MPa H_2 Gas	113 109	S.Z. D.F.
L-H-G	10.5 6.82	20MPa H_2 Gas	110 100	S.Z. D.F.

S.Z.: Stretch Zone, D.F.: Ductile Fracture, Q.F.: Quasi-cleavege Fracture

Table 7. Rising load test results of low toughness weld metal at 150ºC.

T.P.No.	Hydrogen content after test (ppm)	Test Environment	K_{IH} (MPa√m)	Fracture Appearance
L-N-A	—	Air	—	S.Z. D.F.
L-H-A	9.04 9.77	Air Air	No Deviation Point	S.Z. D.F.
L-N-G	— —	20MPa H_2 Gas	70 67	Q.F.
L-H-G	9.60 9.67	20MPa H_2 Gas	86 81	Q.F.

S.Z.: Stretch Zone, D.F.: Ductile Fracture



Pre C.: Pre Crack, S.Z.: Stretch Zone, P. C.: Propagated Crack, D.F.: Ductile Fracture, Q.F.: Quasi-cleavege Fracture

Fig. 12. SEM image of fracture surface of L-H-G. (a) at R.T.; (b) at 150ºC.

Low toughness weld metal was also that standard condition was used one specimen but other conditions were used two specimens (N1, N2) in order to confirm repeatability of the test. K_{IH} values of low toughness weld metal were summarized in Table 6 and 7. The results had almost same tendency of that of high toughness weld metal. In the case of L-H-G condition, K_{IH} values were remarkably decreased and quasi-cleavage was observed in fracture surface as shown in Fig. 12. However K_{IH} value increased and also fracture morphology was changed from quasi-cleavage to ductile fracture due to increase test temperature because of test temperature. It is evident that the effect of dissolved hydrogen on hydrogen embrittlement was a little, whereas hydrogen gas environment acts as the embrittlement factor in this condition. However the effect might be decreased due to increasing metal temperature. Furthermore, the detail of difference between high and low toughness weld metal is described below.

3.4. Holding load test results

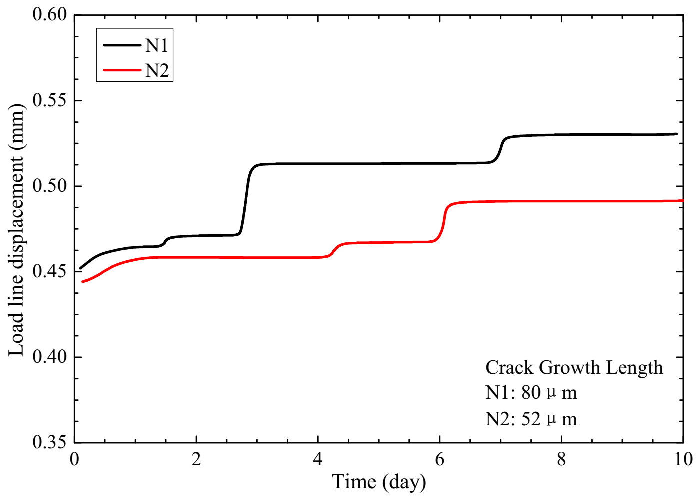


Fig. 13. Holding load test results of high toughness weld metal at R.T. under 20MPa H_2 Gas.

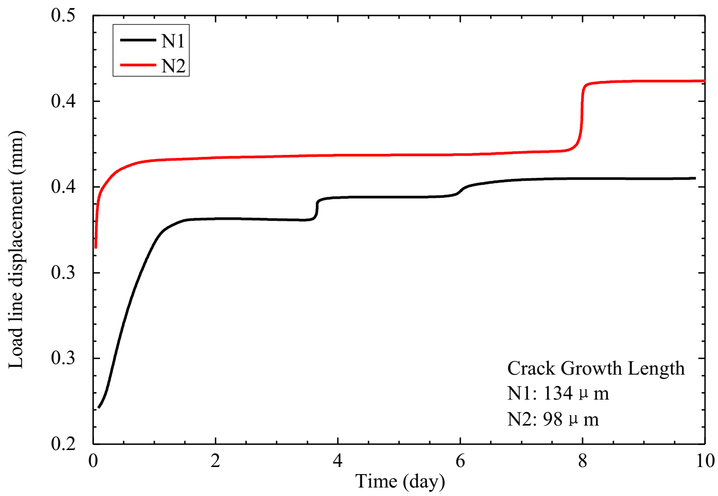


Fig. 14. Holding load test results of low toughness weld metal at R.T. under 20MPa H_2 Gas.

Figure 13 shows holding load test results of high toughness weld metal and crack growth length after 10 days. From this result, it is clear that crack growth occurred at K_{IH} load. In addition, load line displacement changed discontinuously. It is considered that this phenomenon is related to hydrogen accumulation at crack tip but it needs more detail examination of fracture surface. Fig. 14 shows holding load test results of low toughness weld metal and crack growth length after 10 days. Result of low toughness weld metal was almost same as that of high toughness weld metal. Crack growth was confirmed at this load and load line displacement changed discontinuously. From SEM observation, propagated crack was quasi-cleavage and crack growth was also confirmed at K_{IH} load. The difference between high and low toughness weld metal is crack growth length. Crack growth length of low toughness weld metal was longer than that of high toughness weld metal. Thus, it is estimated that low toughness weld metal had a tendency that crack growth occurred easily at K_{IH} load.

4. Discussion

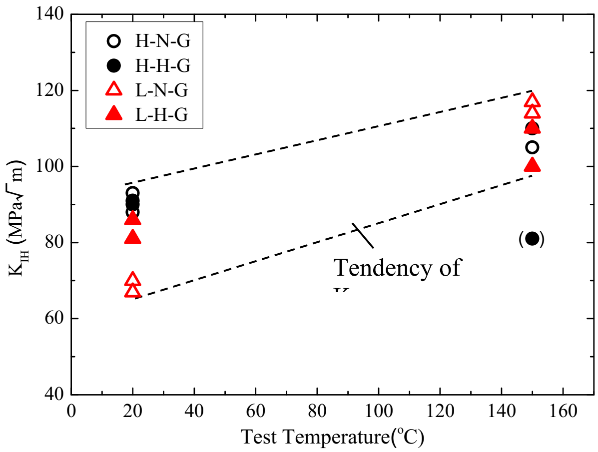


Fig. 15. Relationship between K_{IH} and test temperature under 20MPa H_2 gas.

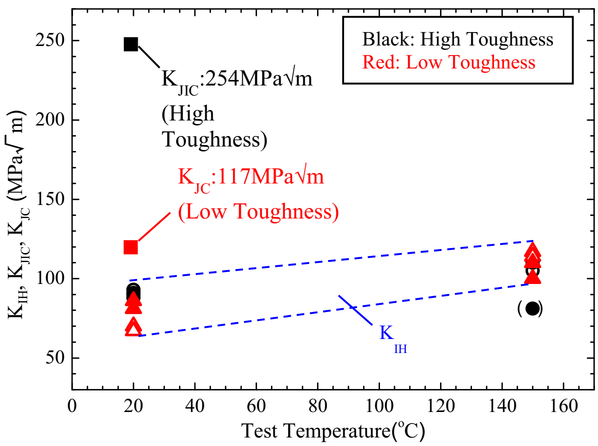


Fig. 16. Fracture toughness values of high and low toughness weld metal.

Figure 16 shows relationship between K_{IH} and test temperature under 20 MPa hydrogen gas condition. Additionally, tendency of K_{IH} values for test temperature is shown in Fig. 15. Although K_{IH} value of high toughness weld metal was higher than that of low toughness weld metal at R.T., K_{IH} value of low toughness weld metal rise to the similar level of high toughness weld metal at 150ºC. It is also to be noted that minimum K_{IH} value can be estimated 60 MPa $\sqrt{}$m at R.T. The reason why K_{IH} become similar level between high and low toughness weld metal at 150ºC is related to toughness at test temperature. Fig. 6 shows transition curve of high and low toughness weld metal.

On the other hand, fast fracture was occurred in low toughness weld metal at R.T. under 20MPa hydrogen gas condition. Fig. 17 shows fracture toughness value (K_{JIC}, K_{JC}) of high and low toughness weld metal. K_{JIC} of high toughness weld metal was 254 MPa $\sqrt{}$m, whereas K_{JC} of low toughness weld metal was 117 MPa $\sqrt{}$m. From these results, fracture toughness value (K_{JIC}, K_{JC}) varied greatly between high and low toughness weld metal.

5. Conclusion

In this study, it was clear that the effect of hydrogen charge and hydrogen gas environment on the embrittlement of 2.25Cr-1Mo-V steel weld metal. The conclusions are described below:

(1) Hydrogen gas affected on the embrittlement of the 2.25Cr-1Mo-V steel weld metal. In contrast, dissolved hydrogen affected little on the embrittlement of the weld metal.

(2) Deviation point of high toughness weld metal was almost same at R.T. and 150ºC under hydrogen gas environment. However propagated crack morphology was changed from quasi-cleavage to ductile fracture at 150ºC.

(3) Deviation point of low toughness weld metal was increased with increasing test temperature under hydrogen gas environment. In addition, propagated crack morphology was changed from quasi-cleavage to ductile fracture at 150ºC. This tendency was almost same as high toughness weld metal.

(4) K_{IH} value of high toughness weld metal was higher than that of low toughness at R.T. However K_{IH} value of low toughness weld metal rise to the similar level of high toughness weld metal at 150ºC

(5) From holding load test results, it was evident that crack growth occurred at the load equivalent to K_{IH}, which obtain by rising load test, for high and low toughness weld metal.

Acknowledgements

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